Icarus **147**, 68–78 (2000)
doi:10.1006/icar.2000.6437, available online at http://www.idealibrary.com on IDEAL®

Iron(VI): Hypothetical Candidate for the Martian Oxidant

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Received November 3, 1999; revised April 14, 2000

As a result of the Viking missions of the early 1970s, the presence of a strong oxidant in martian soil was suggested. Here we present a hypothesis, testable by near-term missions, that iron(VI) is a likely contributor to the martian oxidative pool. In this context, ferrate(VI) salts, with FeO_4^{2-} anion, were studied for their spectral and oxidative properties. Ferrate(VI) has distinctive spectroscopic features that make it available for detection by remote sensing reflectance spectra and contact measurements via Mössbauer spectroscopy, and the relevant miniaturized instrumentation has been developed or is under way, while for the returned samples XANES spectroscopy is shown to be a method of choice. Ferrate(VI) is capable of splitting water to yield molecular oxygen, and oxidizing organic carbon into CO_2. These activities were strongly abated after treatment at elevated temperatures, similar to observations with martian soil samples in the Viking mission. © 2000 Academic Press

1. INTRODUCTION

The program of Mars exploration for the next decade (Mars Surveyor Program, MSP) includes several missions at about two-year intervals. They will involve collection of samples from the martian surface. In these missions, including the Mars Sample Return (MSR), some measurements of physical, chemical, and geological properties of Mars will be completed by both *in situ* studies of the surface and the atmosphere and analyses of returned samples. Key among the investigations, however, will be the search for life in the Universe, with particular focus on Mars, given its planetary history and its proximity to Earth. Mostly due to the Viking missions in the 1970s and more recent Pathfinder investigations, considerable knowledge has been acquired on the geology and chemical composition of Mars (Banin *et al.* 1992, McSween *et al.* 1999). The “biological” experiments on the Viking landers (Oyama *et al.* 1976, Levin and Straat 1976, McKay *et al.* 1998) revealed unexpected chemical activity in the surface material, which in some ways resembled biology but was eventually assigned to a rather complex chemistry. These experiments showed that humidifying martian soil resulted in oxygen evolution, while addition of a bacterial nutrient solution (^{14}C-labeled formate, glycine, lactate, alanine, and glycolate) resulted in $^{14}CO_2$ evolution in the reaction chamber, together with some formation of oxygen. Actually, the phenomena observed in several series of these experiments were rather complicated. Carbon dioxide was released in long-term experiments, but absorbed at the beginning of the exposure of the soil samples to the nutrient solution. Absorption of oxygen was also recorded in some experiments. Release of CO_2 was inhibited almost completely after the “sterilizing” of the martian soil sample at 160°C for 3 h, while O_2 formation remained largely unaffected. These observations were interpreted as indication of the presence of a strong oxidant on the martian surface or, most probably, several different types of oxidants (Klein 1978, Zent and McKay 1994, McKay *et al.* 1998). Samples of terrestrial soils from locations around the world were used to test Viking equipment. Nowhere on Earth was an oxidant present that would be capable of decomposing water. This is not unexpected, taking into account the abundance of reductants that make unlikely the accumulation of such a strong oxidant anywhere on the surface of the Earth.

Given that the martian oxidant is apparently incompatible with either liquid water or organic carbon, it is important to understand its likely abundance and distribution pattern. Is this oxidant located only near the surface, or does it extend deep into the martian soil? Is it distributed uniformly, or can areas without oxidant at all be located (e.g., polar areas)? The answers to these questions are of paramount interest for choosing landing sites

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for MSR, for selecting samples for return, and for the entire program of Mars exploration.

Several candidates have been proposed for the role of martian oxidants: iron oxides (possibly γ-Fe_2O_3), hydrogen peroxide, and other active oxygen species, such as superoxide radical ions, which can be formed due to the UV irradiation of martian surface (Bullock *et al.* 1994, Hunten 1979, Huguenin *et al.* 1979, Levin and Straat 1981, McDonald *et al.* 1998, Yen 1999).

Recently, it was shown that titanium dioxide adsorbs hydrogen peroxide on its surface, and the resulting system can mimic Viking experiments under laboratory conditions fairly well (Quinn and Zent 1999). It is assumed that titanium, most likely in the form of its dioxide, combined in rocks with other oxides, is present in martian soil. Indeed, Banin *et al.* (1992) have estimated its abundance at approximately 0.6 mass%. On the other hand, iron, which has variable oxidation states, is in great abundance in martian soil (third most abundant element, after oxygen and silicon, about 18 mass% on Fe_2O_3 basis). As is well known, the very color of the planet is due to iron oxide(s).

Iron typically occurs as a free metal, or in the oxidation states Fe(II) or Fe(III). However, under certain conditions, higher oxidation states of iron can be formed, as Fe(IV), Fe(V), and Fe(VI) (Turova 1997). Out of these, Fe(IV) and Fe(V) are unstable and decompose (dismutate) into Fe(III) and Fe(VI) under most conditions, and they will not be considered here. However, iron(VI), known in the form of several ferrate(VI) salts, is known as a very strong oxidant and as a well-characterized chemical species. While ferrate(VI) salts are unstable under present conditions on Earth, they are stable enough under some conditions that are consistent with our knowledge of martian soil.

Formation of ferrate(VI) as a purple by-product, in some strongly alkaline solutions, was first described as early as 1702 (Stahl 1715). More recently, ferrates(VI) with various cations, such as potassium, sodium, barium, lithium, rubidium, cesium, silver(I), and even a few tetralkyl/aryl ammonium salts, have been described (Thompson *et al.* 1951, Delaude and Laszlo 1996, Malchus and Jansen 1998, Kulikov *et al.* 1999). Well-characterized potassium ferrate(VI), K_2FeO_4, has been prepared as dark purple, almost black, crystals, decomposing starting at ca. 200°C with oxygen release (Thompson *et al.* 1951). Currently, there is interest in ferrate(VI) as a promising oxidizing reagent for organic synthesis (Delaude and Laszlo 1996, Johnson and Hornstein 1996) and a material for rechargeable alkaline batteries of increased capacity (Licht *et al.* 1999).

Here we present data on ferrate(VI) spectral characterization and chemical activities under the conditions pertaining to the Viking "biological" experiments.

2. EXPERIMENTAL

2.1. Ferrate(VI) Preparation

Several procedures have been described for the synthesis of ferrate(VI): (a) electrochemical oxidation of iron anode (Denvir and Pletcher 1996); (b) calcination of a mixture of ferric oxide with potassium peroxide in a stream of oxygen gas (Dedushenko *et al.* 1989); and (c) wet oxidation of Fe(III) to Fe(VI) by hypochlorite or hypobromite in a highly basic solution (Thompson *et al.* 1951). The last approach seems most practical for preparation purposes, and we used it in our experiments, essentially as outlined by Delaude and Laszlo (1996). First, a concentrated solution of potassium hypochlorite, KClO, was formed by bubbling chlorine gas into cold 10 M KOH solution. The potassium chloride by-product precipitated upon addition of an excess of solid KOH and was removed by vacuum filtration. The addition of small amounts of $Fe(NO_3)_3 \cdot 12H_2O$ to this cold solution resulted in a dark purple mixture as ferrate dianions, FeO_4^{2-}, formed, according to the following scheme:

$$2Fe^{3+} + 3ClO^- + 10OH^- \rightarrow 2FeO_4^{2-} + 3Cl^- + 5H_2O.$$

Solid potassium hydroxide was added again to this dark purple solution, precipitating potassium ferrate(VI), which was then separated by vacuum filtration through a coarse glass filter. The black crystals thus produced were washed with few portions of cold hexane and diethyl ether to remove traces of water (crucial to the stability of the product) and were stored in a dessicator over KOH pellets. Barium ferrate was prepared in an essentially the same way, except that commercial bleach (sodium hypochlorite solution) was added instead of potassium hypochlorite, and barium oxide was added at the final stage of the procedure, to precipitate very low soluble red crystals of barium ferrate monohydrate, $BaFeO_4 \cdot H_2O$.

Total iron in these preparations was determined by standard methods using absorption spectrum of Fe(II)–1,10-phenanthroline complex, while iron(VI) was estimated by the reaction with an excess of chromium(III) nitrate in alkaline solution:

$$\begin{aligned} &Cr(OH)_4^- + FeO_4^{2-} + 3H_2O \\ &\quad \rightarrow Fe(OH)_3(H_2O)_3 + CrO_4^{2-} + OH^-. \end{aligned}$$

Chromate was converted into dichromate by acidification, and the latter was titrated by a standard solution of ferrous sulfate with sodium diphenylamine sulfonate redox indicator (Schreyer *et al.* 1951). The results were compared with the optical absorption of the product in its absorption peak of 507 nm, taking 1100 M^{-1} cm^{-1} for ferrate(VI) dianion molar extinction (1030 M^{-1} cm^{-1} at 505 nm, according to Carr *et al.* (1985)). Nearly 90% purity was attained, according to these measurements, for potassium ferrate(VI).

2.2. Spectral Characterizations

UV-visible absorption spectra of ferrate(VI) solutions in 10 M KOH were recorded using a diode array spectrophotometer HP 8453.

Visible and IR reflectance spectra were measured on both a Beckman 5240 and a Pima (Integrated Electronics) instrument.

X-band EPR spectra were recorded from potassium ferrate powder and solutions at 300 and 77 K, using a Bruker ESP-300E instrument operating at 100-kHz modulation frequency, and with microwave power below the level of saturation.

Mössbauer spectra were recorded at 300 K in zero magnetic field using a conventional constant acceleration spectrometer (Ranger Scientific) with a 1024-channel pulse height analyzer and a Kr gas proportional counter. ^{57}Co in a rhodium matrix was used as a radiation source, and isomer shifts were estimated with respect to metallic iron at 22°C. All spectra were measured in helium gas flow. Powdered samples were sandwiched between two Kel-F plastic holders (Teflon-like material) and were measured immediately. The Kel-F holders appear to be non-reactive with the Fe(VI) sample during the measurement as evidenced by the observation that after the sample and cell were removed from the spectrometer neither the sample nor the Kel-F cell showed any discoloration that might have indicated an alteration reaction with the Fe(VI) sample. However, after several days in contact with the Kel-F holder, severe discoloration and physical alteration of the holder were apparent.

Magnetic hysteresis loops (magnetization versus magnetic field) at room temperature and in fields up to 1.5 T were measured using a vibrating sample magnetometer. About 100 mg of fresh sample was placed in a small plastic capsule and was measured immediately. The time for a complete hysteresis measurement was 15 min.

X-ray absorption near-edge spectra (XANES) were obtained using the Material Research Collaborative Access Team Sector at the Advanced Photon Source, Argonne National Laboratory.

2.3. *Studies of the Chemical Reactivity of Ferrate*

Gases released in the reactions of ferrate(VI) with ordinary water and $H_2{}^{18}O$, and with aqueous solutions of organic compounds, were analyzed in two ways.

The first was with a Micro-Oxymax close-circuit respirometer (Columbus Instruments) designed to detect low levels of oxygen and/or carbon dioxide production/consumption. The volumes of gases are automatically normalized to standard temperature and pressure.

The second was with a Varian Saturn 2000 GC-MS instrument equipped with a Supelco Carboxen 1010 PLOT capillary column, 0.32 mm i.d. and 30 m length. The temperature program started with the temperature of 35°C held for 5 min, then increased to 150°C at 20°C/min. Helium was used as a carrier, at a flow rate of 1.5 mL/min. The mass spectrometer collected data for a mass range of 10 to 100 amu.

All reactions were conducted at room temperature (ca. 25°C) if not stated otherwise. When water was added to the solid potassium ferrate, a considerable amount of heat was released. The mixture was immersed in a room-temperature water bath, in MS related experiments, while no attempt to thermostabilize the mixture was made in respirometer-bound experiments.

The following substrates were used in the reactions with ferrate:

1. Pure water was applied to ferrate in two ways. First, water was placed in an open beaker in the respirometer chamber, while solid ferrate(VI) was kept in the same chamber without direct contact with liquid water. Under these conditions, the reaction could only proceed with water vapor, and its kinetics were limited by the transfer process. Second, water was injected as a liquid to the chamber containing solid ferrate(VI) through a septum using a syringe.
2. A 1 M formic acid solution was applied to solid ferrate(VI) in the same way described above, i.e., using a syringe.
3. A nutrient solution containing a mixture of ca. 0.24 M of the substrates alanine, glycine, lactate, formate, and glycolate (pH was adjusted to pH 8 with 0.5 M NaOH) was applied via syringe.
4. The same nutrient solution, in which pH was adjusted to pH 6 with 2.4 M formic acid, was applied via syringe.
5. The same solutions described in 3 and 4 were used but containing additionally 0.024 M ascorbate.

In several control experiments, potassium ferrate was replaced with a mixture of iron(III) oxide and solid KOH. This mixture was ground, pre-heated at 180°C for 20 min, and then ground again to form a thin powder.

Thermal decomposition of the material was studied by means of differential scanning calorimetry (Shimadzu DSC-50, 5°C/min heating rate, aluminum hermetically sealed sample holder) and thermal gravimetric analysis (Shimadzu TGA-50, 5°C/min heating rate, platinum sample holder, N_2 atmosphere), all in a dry-box.

3. RESULTS AND DISCUSSION

Assessing the possible role of ferrate(VI) as an oxidant on the Mars surface, we address the following questions:

(1) Is there an opportunity to form ferrate (VI) on Mars, according to what is presently known about its surface composition and environmental conditions?

(2) Would such a compound be stable enough to persist and accumulate under those conditions?

(3) Would it be able to display the essential reactivity that was found in the samples of martian soil in Viking experiments, i.e., to produce oxygen gas while moisturized?

(4) Would it produce carbon dioxide while contacting with organic materials that constituted nutrient solution in those experiments?

(5) Would these chemical activities be impaired by heating in a way similar to the heat inactivation employed in the Viking experiments?

(6) Having in mind Mars exploration programs, what are the possible approaches for identification of ferrate(VI), and in particular what are the spectral features of this species that permit

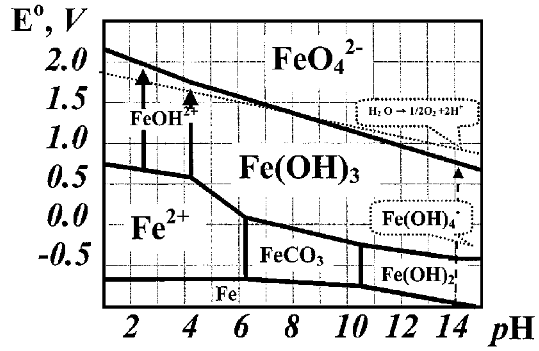

FIG. 1. Approximate pH–E^o diagram of the most abundant iron compounds. Ferrate(VI) occupies the upper-right part of the diagram.

its characterization by both contact measurements and remote sensing?

3.1. *On the Formation and Persistence of Ferrate(VI) in Martian Soils*

The usual way to produce ferrate(VI), accepted as a synthetic approach in most relevant studies, is via wet oxidation of Fe(III) with hypochlorite, as in these experiments. However, formation of ferrate(VI) under dry, elevated-temperature reactions of iron-containing materials with some peroxides has been reported (Kopelev *et al.* 1992, Dedushenko *et al.* 1997). On the other hand, there is a strong belief that active oxygen species, peroxides, superoxides, hydroxyl radicals, and ozone are formed under UV irradiation in the martian atmosphere and affect its soil (Bullock *et al.* 1994, Huguenin *et al.* 1979, Hunten 1979, McDonald *et al.* 1998). Overall, the martian atmosphere is highly oxidized, with domination of carbon dioxide and presence of some dioxygen. Under these conditions, ferrate(VI) could serve to stabilize and store active oxygen, if its decomposition is slow enough to permit the accumulation of the ferrate. We do not specify, at this point, if such an iron form is merely a surface compound, or if it is present also at some depth in martian soil, though the former situation looks more likely, taking into account the rather low content of oxidant in samples taken by Mars landers.

Ferrate(VI), when in liquid phase, is rather stable in strongly alkaline solutions only, at pH > 10, and even under these conditions it is readily reduced by most organic materials. In a pH–E° diagram, where E° is the oxidation potential of the system, the stability region can be approximately presented as shown in Fig. 1. In constructing this diagram, by extending that published earlier by Stumm and Morgan (1970), we took into account that the reduction potentials for the Fe(VI)/Fe(III) couple have been estimated as 2.20 and 0.72 V vs NHE in acidic and basic solutions, respectively (Wood 1958), according to the equilibria

$$FeO_4^{2-} + 8H^+ + 3e^- \Leftrightarrow Fe^{3+} + 4H_2O$$

$$FeO_4^{2-} + 4H_2O + 3e^- \Leftrightarrow Fe(OH)_3(s) + 5OH^-.$$

At lower pH, both organic materials and water are oxidized. So, thermodynamically, one would need a highly alkaline environment for ferrate(VI) to be stored. This requirement is not so limiting for martian soil, as it might seem at first glance. Indeed, there are strong reasons to assume that in the absence of biogenic calcium carbonate deposits, which now serve as a powerful buffer on the Earth's surface, both pre-Cambrian Earth and Mars at some stage of its geological history were covered with a "soda ocean" with pH > 9 (Kempe and Degens 1985, Mills and Sims 1995).

While other (more acidic) scenarios have been suggested for Mars (Burns and Fisher 1993), in the absence of conclusive pH measurements, the only experimental evidence now available (Klein 1978) favors the alkaline environment: solutions produced by mixing the samples of martian soil with water displayed a short-term absorption of carbon dioxide, as any basic solution would do. From simulation experiments, Quinn and Orenberg (1993) also concluded that martian soil material is most likely at least mildly alkaline.

Ferrates of alkaline metals are unstable in the presence of moisture. However, the martian surface is dry and cold and even alkaline ferrates can be stabilized there. Other ferrates, such as barium ferrate(VI), are much less water soluble and are consequently fairly stable in a humid milieu. Furthermore, ferrate(VI) anions are not sensitive to light (UV or visible) (Wagner *et al.* 1952). Overall, the formation of ferrate(VI) and its preservation in soil are consistent with present knowledge of the chemical composition and environmental conditions at the martian surface.

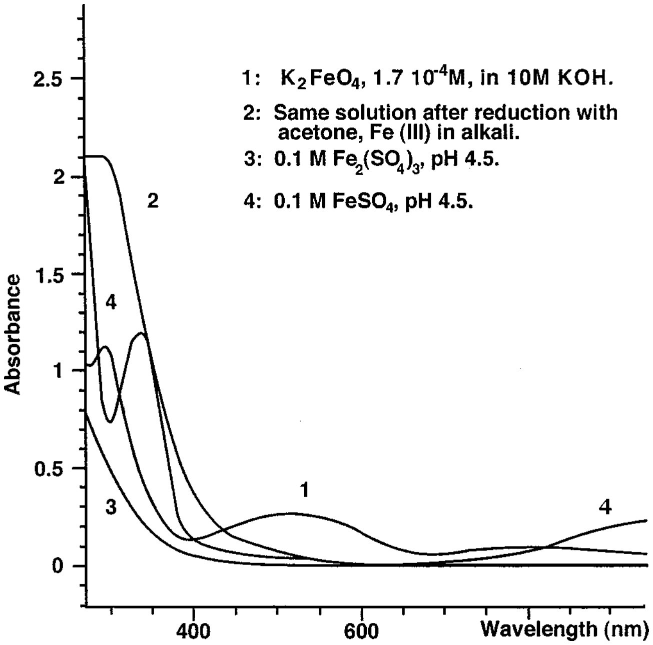

FIG. 2. Visible absorption spectra of iron compounds in solutions. (1) K_2FeO_4, $1.7 \cdot 10^{-4}$ M, in 10 M KOH. Characteristic peak at 507 nm, $\varepsilon_{507} = 1100$ M^{-1} cm^{-1}. (2) Same solution after reduction with acetone. (3, 4) Iron(III) and iron(II) sulfate solutions.

3.2. Spectral Characterization of Ferrate(VI)

3.2.1. Absorption and reflectance spectra. A deep purple color appearing in iron-containing highly alkaline solutions when treated with strong oxidants was found centuries ago (Stahl 1715). This characteristic color is due to the tetrahedral ferrate(VI) dianion, FeO$_4^{2-}$, with its absorption peak at 505–510 nm, as shown in Fig. 2, and a molar extinction of 1100–1300 M^{-1} cm^{-1} at these wavelengths. This spectrum makes ferrate(VI) very distinct from other forms of dissolved iron, and makes the absorption spectrum an appropriate tool for ferrate(VI) identification and quantitation when samples are available for dissolution.

With Mars exploration in view, a more practical approach might be to utilize reflectance spectra that can be recorded by remote sensing from orbit. The broad-range reflectance spectrum of crystalline potassium ferrate, together with other forms of iron and their mixtures, is presented in Fig. 3. The band at 1.6 μm is a characteristic one, and it can be used as a marker to search for the presence of Fe(VI) on the martian surface. Reflectance spectra in a more narrow visible range are also included in Fig. 3. They show general correspondence with the absorption spectra in Fig. 2 and are also quite distinct from other forms of iron.

According to Viking's results, the content of oxidant in martian soil should be rather low, most likely in ppm range. If this reactive material were the only one with ferrate(VI) spectral features, it certainly would not be visible in reflectance spectra. However, we now know that combinations of ferrate(VI) anion with various metal cations may considerably differ in both their water solubility and their reactivity. Most of the ferrate(VI), if present at all, may be in the form of some non-reactive compounds, of which barium ferrate is an example. Though chemically rather resistant, they still give the characteristic peak at ca. 1600 nm, making the detection of ferrate(VI) likely by means of remote sensing reflectance spectroscopy.

3.2.2. Mössbauer spectra and magnetic measurements. Mössbauer spectroscopy is probably the most powerful and straightforward approach to the identification of various oxidation states of iron. It is especially important in the context of these studies since a compact Mössbauer instrument has been developed for the future Mars missions and is proposed as a part of the Athena payload (Klingelhöfer *et al.* 1996, Klingelhöfer 1999). The room-temperature Mössbauer spectrum of a sample containing potassium ferrate(VI), together with other iron species, is shown in Fig. 4, together with a diagram of the ranges of isomer shifts in iron compounds with various valences and spin states, as referenced to iron metal at 300 K. It is produced

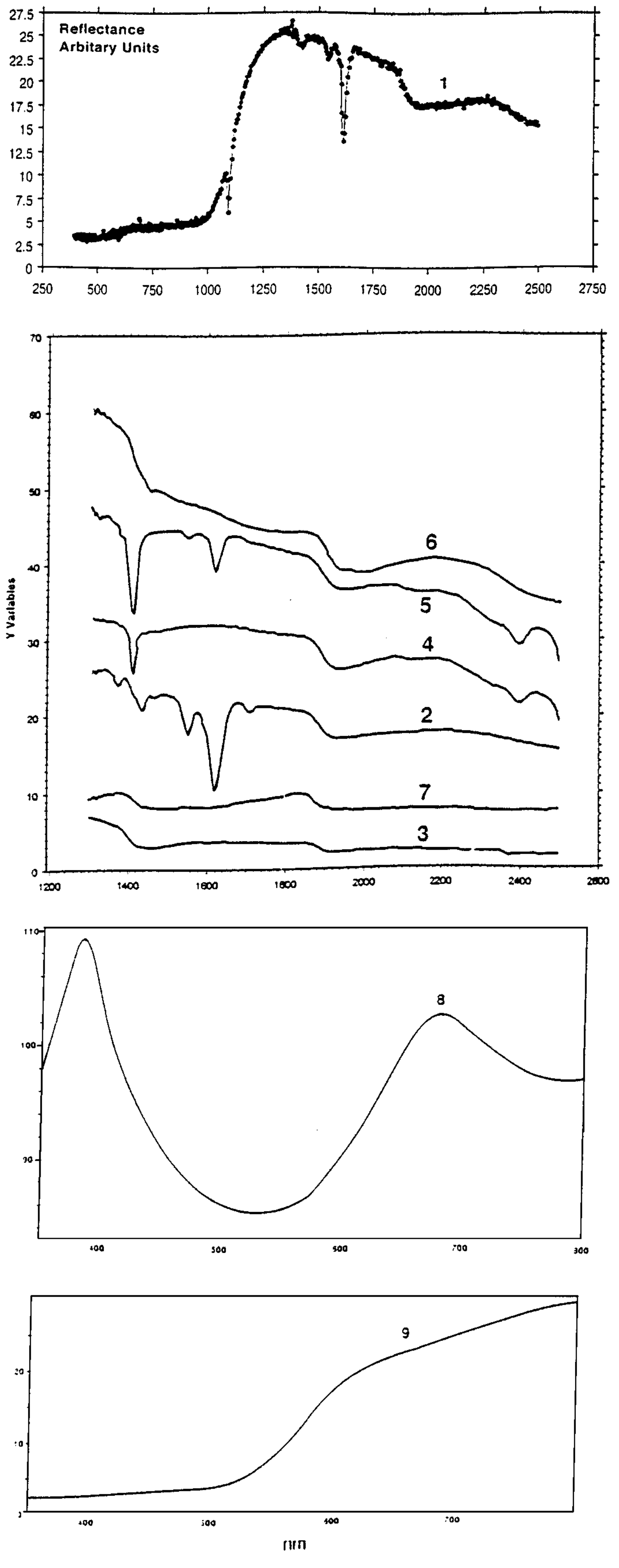

FIG. 3. Reflectance spectra of iron compounds. (1) Broad-range spectrum of solid potassium ferrate; (2–7) spectra in the range 1200–2400 nm. (2) Solid K_2FeO_4. (3) Fresh moisturized precipitate of Goethite, FeOOH. (4) CaO–Fe_2O_3 mixture, 10 : 1 by mass. (5) CaO–Fe_2O_3–K_2FeO_4 mixture, 20 : 2 : 1 by mass. (6) Solid $FeSO_4$. (7) Solid $Fe_2(SO_4)_3$. (8, 9). Visible-range reflectance spectra. (8) CaO–Na_2FeO_4 mixture. (9) Al_2O_3–F_2O_3 mixture.

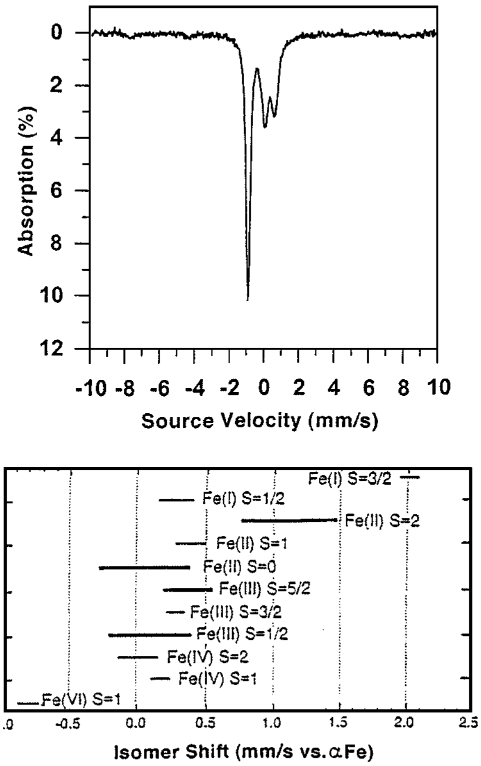

FIG. 4. Mössbauer spectrum of ferrate(VI)–Fe_2O_3 mixture, and the diagram (Fultz 1999) of typical isomer shifts for iron compounds with various valences and spin states, as referenced to αFe at 300 K.

by a superposition of two main spectral components. One component consists of a singlet line with a negative isomer shift of -0.91 mm/s, and the other is a quadrupole-split doublet with an isomer shift of $+0.32$ mm/s and quadrupole splitting of 0.57 mm/s. The relative abundance of these two components was estimated from the relative area of the two sub-spectra, and it indicated that the singlet component accounted for 48% of the total area.

The singlet component has a negative isomer shift, which is opposite in sign to the isomer shifts for Fe(II) and Fe(III) phases. This component is identified as the primary Fe(VI) phase, and its isomer shift is slightly more negative than previously reported for this compound (Wertheim and Herber 1962). A negligible quadrupole splitting is expected for Fe(VI) in K_2FeO_4 based on its $3d^2$ electronic configuration in a tetrahedrally coordinated site. The doublet component has an isomer shift and quadrupole splitting consistent with an Fe(III)-bearing phase which is paramagnetic at room temperature.

In addition to the two main components, a barely discernible magnetically split sextet was also observed (Fig. 4) with a magnetic hyperfine field of 49.7 T. The full sextet hyperfine spectrum is observed in magnetically ordered materials when the atomic magnetic moments are fixed in space for a time greater than 10^{-9} s. The presence of a magnetically ordered phase was also confirmed from the room temperature magnetization measurements. At room temperature, the field-dependent magnetization approaches saturation but shows no hysteresis, typical of superparamagnetic behavior exhibited by nanophase iron-oxide magnetic materials (grain size <30 nm). From the bulk value of saturation magnetization ($M_s = 0.325$ Am^2/kg), the iron-oxide phase is most likely a strongly magnetic phase such as magnetite ($M_s = 92$ Am^2/kg) or maghemite ($M_s = 75$ Am^2/kg) rather than a weakly magnetic phase such as hematite ($M_s = 0.4$ Am^2/kg) or an iron oxyhydroxide phase. Otherwise, the hematite/Fe-oxyhydroxide phase would be over 90% of the sample by weight and would readily be detected with Mössbauer. Assuming the phase is magnetite or maghemite, the bulk M_s value indicates that this phase is about 0.4% by weight consistent with the weak sextet sub-spectra observed in Fig. 4. It also shows that the Mössbauer spectrum of Fe(VI) can be easily detected in the presence of iron in other oxidative states.

3.2.3. EPR spectra. Ferrate(VI), with its sd^3 hybridized iron, and $3d^2$ electron configuration, is paramagnetic and EPR active. Electron paramagnetic resonance spectra of magnetically diluted oriented single crystals of several salts of general formula K_2MO_4 (M = S, Cr, Se), isomorphously doped with FeO_4^{2-} anions, have been previously published and theoretically analyzed in detail (Abdulsabirov *et al.* 1979, Wagner *et al.* 1995). Non-oriented powder samples display a singlet EPR spectrum at $g \approx 1.9948$, with a line-width of ca. 8 mT at 77 K, which is significantly broadened at room temperature (Fig. 5). This, again, opens an opportunity for searching for Fe(VI) in future Mars missions, since the development of a miniaturized EPR instrument is underway (Kim *et al.* 1997).

3.2.4. X-ray spectra. XANES spectra of a ferrate(VI) sample are shown in Fig. 6. In this technique, the focus is on the region very close (within about 30 eV) to the ionization threshold of the compound in question. The structure of the absorption spectrum in this region is very sensitive to the three-dimensional geometry of the atoms surrounding the excited iron atom. Comparison of XANES spectra of a sample with XANES spectra of known standards allows identification of the oxidation state and local geometry around iron. For iron, the X-ray absorption

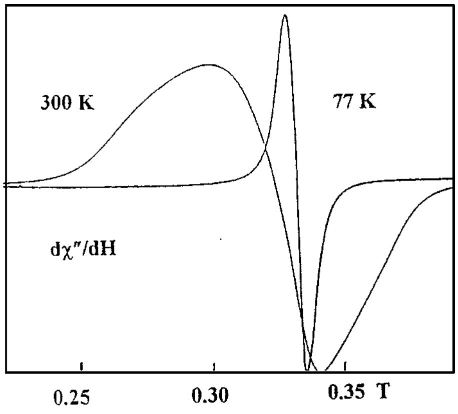

FIG. 5. EPR spectra of powdered ferrate(VI) at 77 K and room temperature.

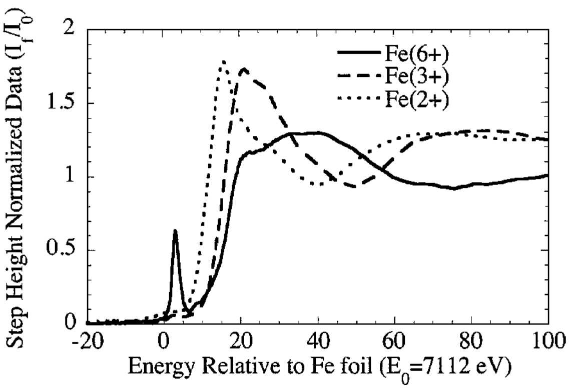

FIG. 6. XANES spectrum of ferrate(VI) solution, as compared to iron(III) and iron(II) salts.

edge energy is ~7112 eV, and a characteristic pre-edge feature is observed from both solutions and solid samples containing tetrahedrally coordinated Fe(VI) in the ferrate dianion. Additionally, more subtle changes in X-ray absorption edge energy have been shown to enable the identification of Fe(II) and Fe(III) valence states (a more detailed discussion of the XAS data collection, analysis, and interpretation has been submitted to the *Journal of Synchrotron Radiation*).

3.3. Chemical Reactivity of Ferrate(VI)

3.3.1. Thermal decomposition. In the Viking Gas Exchange Experiments (GEX), it was found that samples of martian soil released oxygen in amounts of 70 to 700 nmol/μL upon introduction of water vapor into the sample cell (Oyama *et al.* 1976, Levin and Straat 1977). Oxygen was released also from a sample of soil that had been pre-heated at 145°C, even though the amount of gas was substantially reduced.

Potassium ferrate(VI) as a dry powder is stable at room temperature. However, upon heating it decomposes, releasing dioxygen. This decomposition proceeds slowly, starting about 50°C and becoming complete by 300°C. Thermal decomposition is a complex, multi-stage process, as can be seen from thermogram and DSC observations (Fig. 7). One may speculate that transient lower oxidation states of iron, such as Fe(+5) and Fe(+4) are first produced before the final product, Fe_2O_3, forms. These intermediate forms will also display high oxidative power. It is expected that thermal stability will be impaired in the presence of traces of water. Catalytic effect of Fe(III) on ferrate decomposition is anticipated and may significantly complicate the results of DSC and thermogravimetry analysis. These results are relevant to both the understanding of Viking data and the treatment of future return samples, since they show that heat "sterilization" of martian soil might result in a set of various iron products in a poorly predictable manner, depending on the other components of the soil and, possibly, on the rate of heating, too.

3.3.2. Water oxidation. Aprotic solvents as ether, chloroform, and benzene are not immediately reactive with ferrate, which permits their application for removal of traces of water from the insoluble ferrate preparation at the final stage of its purification. Though methanol has also been recommended in some publications for water removal, in our hands, its application invariably resulted in partial reduction of ferrate(VI) to iron(III), which is in line with difficulties related to the removal of water traces from this solvent.

Addition of water to potassium ferrate(VI), results in intensive gas evolution. In the Viking experiments, no attempt was made to explore the interaction of soil samples with pure liquid water, although oxygen evolution was observed when water vapor, from the nutrient solution, accessed the solid soil. The nature of the reaction was not explored in detail, and it remained unclear if it was a stoichiometric oxidation of water or a decomposition of the solid material, catalyzed or initiated by water. Water reaction with potassium ferrate, however, is a true water oxidation: GC-MS analysis of the gas product after the reaction of potassium ferrate with liquid $H_2{}^{18}O$ revealed that the gaseous product formed in the head space of the reactor vessel was ${}^{18}O_2$, in accordance with the results published earlier, which indicated little ferrate–water exchange of oxygen. Water oxidation is enhanced at low pH, since the most active oxidizing species is $HFeO_4^-$ anion, not FeO_4^{2-} dianion per se (Goff and Murmann 1971). The reaction may be represented by the following scheme:

$$HFeO_4^- + 1/2H_2O \rightarrow FeOOH + 3/4O_2 + OH^-.$$

Sparingly soluble barium ferrate(VI) monohydrate, $BaFeO_4 \cdot H_2O$, formed by ion-exchange precipitation from a sodium ferrate(VI) solution with barium nitrate, was not reactive under comparable conditions.

We explored the kinetics of dioxygen accumulation in two ways. First, as in Viking experiments, dioxygen formation was measured under conditions where solid potassium ferrate(VI) interacted with water vapor only. In this experiment, liquid water and ferrate were placed in separate open containers in the same chamber of the Micro-Oxymax respirometer. Typical results on the kinetics of dioxygen accumulation under these conditions are presented in Fig. 8A. The reaction develops slowly and steadily, and the kinetics obviously reflects the transfer of vapor to ferrate(VI).

In another series of experiments, potassium ferrate(VI), in the amount of ca. 50 mg was placed in the respirometer chamber, then 0.2 or 2 mL of water was injected, providing direct contact of the solid material with liquid water. In this setting, dioxygen was released immediately (Fig. 8B). The reaction was not significantly impaired by pre-heating the solid potassium ferrate at 145°C, or even at 170°C for 2 h. In that sense, the observations were qualitatively similar to the Viking results, which indicated that dioxygen formation was rather resistant to preheating ("sterilization") of the samples of martian soil.

When water was replaced by a liquid "nutrient solution," i.e., an aqueous solution of a mixture of organic acids, typically a short burst of dioxygen was first observed, though it is a lesser amount than with pure water, but then oxygen consumption was

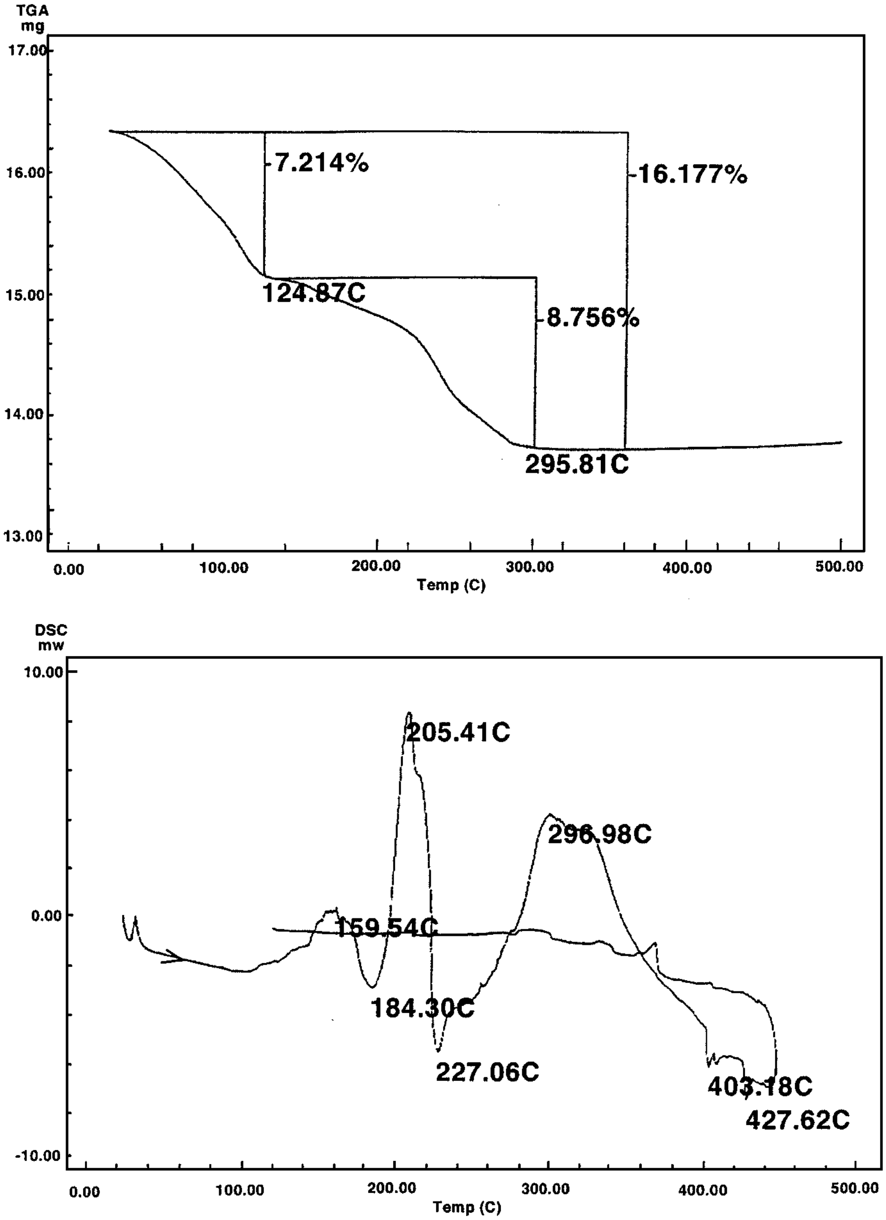

FIG. 7. Thermal decomposition of potassium ferrate(VI) samples: thermogravimetry, starting mass 16.34 mg (top), and DSC (bottom) results. Temperatures marked are upon heating.

recorded (Fig. 8C). More thorough heating, at 185°C for 4 h, resulted in ferrate(VI) decomposition (the color of solid changed drastically from dark purple to greenish) and produced solid material, which was unreactive with water (Fig. 8A, Graph 3, and Fig. 8C, Graph 3). In addition, the mixture of iron(III) oxide with alkali produced no oxygen, and only fluctuations within instrument stability limits of approximately $\pm 50\,\mu$L of gas volume could be seen.

3.3.3. Generation of carbon dioxide from organic material. In the Viking Labeled Release Experiment (Levin and Straat 1976), $^{14}CO_2$ was rapidly released upon contact of the surface material with ^{14}C-labeled nutrient solution. The reaction slowed down after a small fraction of the added organic medium decomposed. Preheating the samples to 160°C for 3 h completely inhibited the release of $^{14}CO_2$ (Levin and Straat 1977).

According to their respective redox potentials, ferrate(VI) is a stronger oxidant than permanganate and chromate (see Table I). The extremely strong oxidizing power of ferrate(VI) has been well documented in its reactions with a number of various compounds: it converts chromium(III) to chromate (Schreyer *et al.* 1951), oxidizes ammonia, cyanide (Sharma *et al.* 1998a, 1998b), hydrogen sulfide, and other sulfur compounds (Johnson and Read 1996, Sharma *et al.* 1997, Read *et al.* 1998, Read and

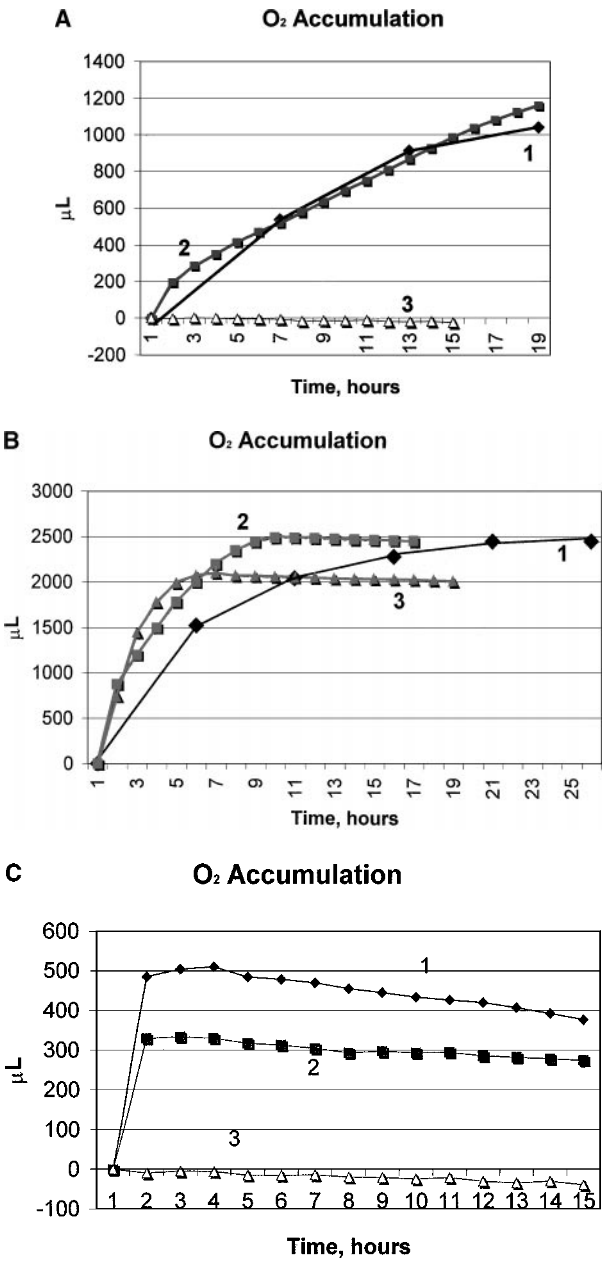

FIG. 8. Accumulation of oxygen gas in the reaction of solid potassium ferrate(VI) with water. (A) 50 mg crystalline K_2FeO_4 was put in the Micro-Oxymax respirometer chamber, and 3 mL water was placed in an open beaker in the same chamber, providing contact through vapor phase only. (1) Control with no pre-heating. (2) Potassium ferrate was pre-heated at 170°C for 3 h. Pre-heating did not prevent oxygen evolution under these conditions. (3) Potassium ferrate pre-heated at 185°C for 4 h. Evolution of oxygen totally suppressed. (B) Two milliliters pure water was injected via syringe through septum in the side-arm of the Micro-Oxymax chamber, to provide direct contact of liquid with solid potassium ferrate. (1) Control with no pre-heating. (2) Solid potassium ferrate(VI) pre-heated at 145°C for 2 h. (3) Pre-heated at 170°C for 3 h. Oxygen release not prevented by this thermal pre-treatment. (C) Oxygen release in the reaction of potassium ferrate (50 mg) with nutrient solution, pH 6 (2 mL) with no pre-heating (Graph 1) and after heating of the solid at 145°C for 2 h (Graph 2) and at 185°C for 4 h (Graph 3).

TABLE I
Standard Potentials, E^o (volts), of a Few Redox Couples in Acidic and Alkaline Solutions

Acidic solution		Alkaline solution	
FeO_4^{2-}/Fe^{3+}	2.20	$FeO_4^{2-}/Fe(OH)_3(s)$	0.78
MnO_4^-/MnO_2	1.68	$MnO_4^-/MnO_2(s)$	0.59
$Cr_2O_7^{2-}/Cr^{3+}$	1.33	$CrO_4^{2-}/Cr(OH)_3(s)$	−0.12

Wyand 1998), and was proposed as a valuable oxidizing reagent for organic synthesis (Delaude and Laszlo 1996) and wastewater treatment (Carr *et al.* 1985).

In our hands, addition of aqueous solutions of formate to powdered potassium ferrate(VI) resulted in the release of carbon dioxide in the head space of the reactor vessel, due to the oxidation of organic carbon (Fig. 9, Graph 1). Formate was chosen for these preliminary experiments because carbon dioxide is the only possible product of its oxidation. Therefore, even visual observations of the change in color (from purple to yellow-brown) served as an unambiguous indication of carbon dioxide formation. When a complete nutrient solution was added to solid ferrate(VI), release of carbon dioxide was recorded as well (Fig. 9, Graphs 2, 3, and 8). However, it was completely inhibited and actually reversed to a steady CO_2 consumption after pre-heating at 145 or 170°C (Fig. 9, Graphs 4–7).

Addition of silicon dioxide had little effect on the oxidation of the nutrient solution by ferrate, although it seemed to slow down the initial burst of carbon dioxide (Fig. 9, Graph 8). At the same time, some dioxygen was also formed in all experiments with diluted nutrient solutions, apparently due to a

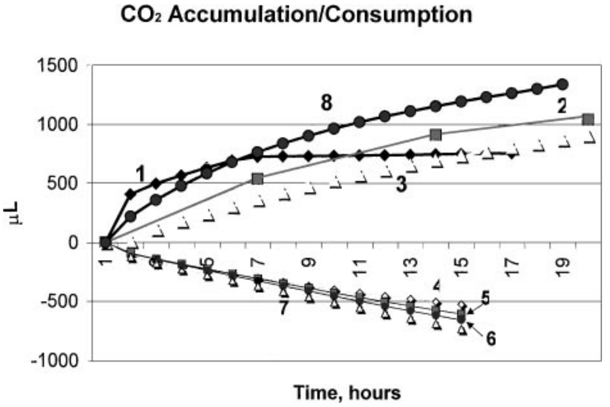

FIG. 9. Release of carbon dioxide at the reaction of solid potassium ferrate(VI) with solutions containing organic acids: (Graph 1) 0.2 mL of 2.4 M formic acid added to 50 mg potassium ferrate; (Graphs 2, 5, 7) 2 mL of nutrient solution pH 6 added to 50 mg solid; (Graphs 3, 4, 6) 2 mL of nutrient solution pH 8 added to 50 mg potassium ferrate; (Graph 8) nutrient solution pH 8 added to a mixture of 50 mg potassium ferrate with 150 mg silica. (Graphs 1–3 and 8) Control with no pre-heating. (Graphs 4, 5) Solid pre-heated at 145°C for 2 h. (Graphs 6, 7) Solid pre-heated at 170°C for 3 h. Both thermal pre-treatments prevented further carbon dioxide formation.

concomitant reaction of ferrate with water. It should be kept in mind that some background carbon dioxide consumption is anticipated in each case due to the alkaline nature of the solid reagent. The balance between oxidation and neutralization reactions may give various net concentrations of carbon dioxide in head space, and in the absence of oxidation (as after thermal treatment of ferrate(VI) steady consumption of CO_2 is actually observed. Again, the product of the ultimate thermal decomposition of potassium ferrate displays essentially the same behavior, in terms of CO_2 consumption, as a mixture of iron(III) oxide and KOH.

While the observations presented here are in line with the results of Viking Labeled Release Experiments some caution needs to be exercised concerning these similarities. The details of the composition of martian soil remain unknown. Thus, neither the way iron(VI), if present, is chemically bound to other oxides nor how such a combination would affect the reactions of ferrate can be predicted. For instance, which cations are likely to participate? We do know that combination with barium oxide (barium ferrate(VI)) is far less reactive than with alkaline ferrates. Besides, our experiments were designed in a way to make measurements convenient and distinctively visible. To this end, e.g., concentrations of “nutrient solutions” were much higher than those in microbiology practice. As a result, all kinetics were completed within several hours. No attempt has yet been made to extend these observations for months as was done in the case of the Viking missions. Experiments with more dilute solutions and different ratios of solid ferrate/solution volume, which gave inconclusive results, approaching the instability limits of the instrument, were not taken into account, and further effort would be necessary for a closer simulation of the original Viking experiments. Nevertheless, the overall set of results, i.e., basically the evolution of oxygen on water vapor–ferrate contact and its relative lack of sensitivity to pre-heating, as well as carbon dioxide release and absorption, together with pre-heating effects, are all in line with the observations made by the Viking landers.

Thus, iron in its higher oxidation states may be considered a plausible contributor to the oxidative pool in martian soil, which is responsible for its self-sterilizing properties. One encouraging note is that our hypothesis is testable, and there are good prospects for testing it in the forthcoming Mars missions, through measurements by both remote sensing and contact experiments *in situ*, and by the analysis of the returned samples.

ACKNOWLEDGMENTS

This work was performed at the Jet Propulsion Laboratory/California Institute of Technology, under contract with NASA, Grant 100483.344.50.34.01. Use of the Advanced Photon Source was supported by DOE, Basic Energy Sciences, Office of Science, under Contract W-31-109-Eng-38. Support was also provided by DOE, Biological and Environmental Research, National Accelerated Bioremediation (NABIR) Program, and National Argonne Laboratory LDRD funds. We thank Cindy Grove and Soon Sam Kim, at JPL, for access to some spectral facilities, and Anna Larsen (Chemistry Department, UC-Riverside) for thermogravimetric and DSC measurements.

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